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# GRANULAR MESOPOROUS ACTIVATED CARBONS FROM WASTE TYRES BY CYCLIC OXYGEN CHEMISORPTION-DESORPTION

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## Abstract

The activation upon cyclic oxygen chemisorption-desorption has proved to be an efficient way for the development of porosity at low burn off from waste tyres char. In this work the influence of particle size, desorption temperature and the number of cycles is studied. Highest values of burn-off and specific surface area ($S_{BET}$) are obtained for the largest particle diameter (3 mm average) and at intermediate desorption temperature (650ºC). In these conditions $S_{BET}$ values around 500 $m^2/g$ can be achieved at burn-offs of about 30%, and close to 600 $m^2/g$ at around 45% burn-off, with a mean pore size of 10 nm and a micropore volume close to 0.08 $cm^3/g$. Although the surface area is moderate, the low burn-off and high $S_{BET}$/burn-off ratio achieved makes possible to maintain initial granular morphology of the particles even after 20 cycles of activation.

**Keywords:** activated carbon, mesoporous, waste tyres, cyclic activation, air activation

## 1. **Introduction**

The preparation of activated carbons is the most studied alternative for the valorization of char obtained from pyrolysis of waste tyres. Most of works are focused in physical activation with steam or $CO_2$ while air or, in general, oxygen mixtures, are much less studied because the high reactivity of oxygen with these chars do not lead to significant porosity generation, but mainly to particle burning. Thus, Helleur et al. [1] reported no significant surface area development ($S_{BET}$) at 15% burn-off using 2/98 (vol) $O_2/N_2$ mixture as activating agent. The existing literature on physical activation of waste tires char shows that it is difficult to achieve $S_{BET}$ values above 300-400 $m^2/g$ without high burn-off. As representative examples of the activation with $CO_2$, previous works reported at 900ºC $S_{BET}$ values between 200 and 300 $m^2/g$ for a 10 – 40 % burn-off, and at 950 – 1100 ºC specific surfaces of 200 – 1100 $m^2/g$ were obtained at burn-off values around 80% [1-3].

Air (oxygen) is by far the less expensive activating agent but its main drawback derives from its high reactivity that seriously difficults an effective control of the activation process which most commonly takes place under diffusion control leading to particle burn-off with a poor development of surface area. Cyclic activation by oxygen chemisorption/desorption has been proposed as an interesting method for a controlled activation that allows tailoring of activated carbons by target porosity development [4]. This method, so far scarcely studied in the literature, can provide an efficient way to create whole porosity from a precursor and to controllably modify the porous structure of a carbonaceous material while maintaining the physical integrity of the particle so that granular activated carbon can be obtained.

In a previous work we studied the activation of waste tyres char upon cyclic oxygen chemisorption-desorption, showing the feasibility of a controlled development of porosity at low burn-off using air as fed gas for the activation process [5]. The first step of each cycle is chemisorption at moderate temperatures (200-250ºC) of the oxygen from an air stream. In the second step, the chemisorbed oxygen is desorbed at higher temperature (500-900ºC) in inert atmosphere, evolving as CO and $CO_2$ and leaving new reactive carbon sites. In successive cycles a moderate but maintained increase of $S_{BET}$ was observed. Initially mainly mesopores were created and afterwards microporosity development began while mesoporosity decreased probably due to mesopores widening. The $S_{BET}$ values achieved even after 15 cycles was moderate (100 – 250 $m^2/g$) but the surface development was associated to low burn-off values (between 6 and 20%) and showed a high contribution of external or non-micropore area (up to 50 % of the BET surface area). The low burn-off values obtained made possible to maintain the initial morphology of the char particles; so that, granular mesoporous activated carbons could were prepared.

From previous results it can be concluded that the desorption temperature and the number of cycles are two of the main important variables of the process. Thus, higher desorption temperatures yields higher burn-off values, higher $S_{BET}$ and lower mean pore size, and a continuous increase of microporosity can be accomplished by increasing the number of cycles.

The aim of this work is to increase the BET surface area maintaining reasonably low burn-off values. The influence of desorption temperature and char particle size is evaluated in

order to identify the operating conditions that can yield activated carbons with a predefined porous structure in the micropore and the mesopore range.

## 2. Materials and methods

Experimental devices and procedures and samples characterization were similar than those used in previous works [5] so that we briefly will summarize in the following.

### *2.1. Preparation of char*

The raw material used was rubber from waste Pirelli P2000 tyres. The rubber was cryogenically grinded in liquid nitrogen and sieved to three different fractions: 1, 2 and 3 mm average particle diameter, named in this study S, M and L, respectively. The char was obtained from pyrolysis of each fraction at 800ºC during 20 min under 100 NmL/min nitrogen flow.

### *2.2. Cyclic activation*

The operating conditions for the chemisorption step of each cycle were the same for all the experiments (210ºC, 3 h, 80 NmL/min air flow) and were determined as the optimum conditions in a previous work (Heras et al 2009). The desorption step was carried out at three different temperatures (550, 650 and 750 ºC) using a flowrate of 100 NmL/min of nitrogen and 2 h of reaction time in all the cases. The resulting samples were identified by S, L and M followed by the desorption temperature in ºC.

*2.3. Characterisation of samples*

The burn-off after each cycle was determined by sample weighting. The $S_{BET}$ and the pore size distribution of the samples were determined from nitrogen adsorption-desorption at 77 K using a Micromeritics TriStar II 3020 apparatus. The $S_{BET}$ was calculated by a Multipoint method while the t-method was used to calculate the micropore volume and external or non-micropore area. Scanning electron microscopy (SEM) was performed in a Hitachi S-3000N device to study changes in morphology.

*2.4. Experimental program*

In a first series of experiments and on the basis of the results obtained in previous works [5], the influence of desorption temperature and particle size was studied using 6-cycles activation tests. The results from the 6-cycles activations tests were processed by means of StatGraphics software to determine the significance of operating variables. Then, three-variable levels combinations that provided convenient results in terms of surface area development were selected for 20-cycles activation tests.

**3. Results**

Figure 1 shows the evolution of burn-off and BET surface area upon the first series of experiments of 6 cycles duration. As can be observed the burn-off increased progressively with the number of cycles. The final values of burn-off obtained were lower than 15% at all the operating conditions tested. The $S_{BET}$ also increased with the number of cycles and after 6 cycles variable values between 110 and 260 $m^2/g$ were obtained, except for the combination of L particle size and 650ºC desorption temperature, which provided a $S_{BET}$ value of 391 $m^2/g$. This combination also yielded the highest burn-off (15%). The values of

the ratio $S_{BET}$/burn-off obtained are in general frankly higher those reported for air activation of waste tyres chars[1], and similar to those obtained by Py et al.[4] using cyclic oxygen adsorption-desorption activation with less reactive precursors such as coal and tar pitch. The development of porosity was accompanied by a monotonical reduction of the mean pore size during the 6-cycle tests (Figure 2). After the first activation cycle a very important reduction of the mean pore size took place in most cases, leading to fairly similar values. In the following cycles a gradual decrease was observed and the differences in mean pore size became higher. Table 1 summarizes the results obtained after completion of the 6 activation cycles. In general, the high burn-off is associated with a higher BET surface area and a lower mean pore size.

**Table** 1**.** Results of activation after 6 cycles.

| | **S550** | **M550** | **L550** | **S650** | **M650** | **M650*** | ***L650*** | ***S750*** | **M750** | ***L750*** |
|---|---|---|---|---|---|---|---|---|---|---|
| **Burn-off (%)** | 11.9 | 7.7 | 9.8 | 14.4 | 12.4 | 12.0 | *15.3* | *15.1* | 11.6 | *13.0* |
| **$S_{BET}$ ($m^2$/g)** | 193 | 111 | 176 | 206 | 248 | 240 | *391* | *255* | 176 | *237* |
| **Dmean (nm)** | 18.6 | 28.7 | 20.0 | 17.8 | 16.6 | 17.0 | *12.1* | *15.7* | 23.4 | *16.3* |

(*) Replicate

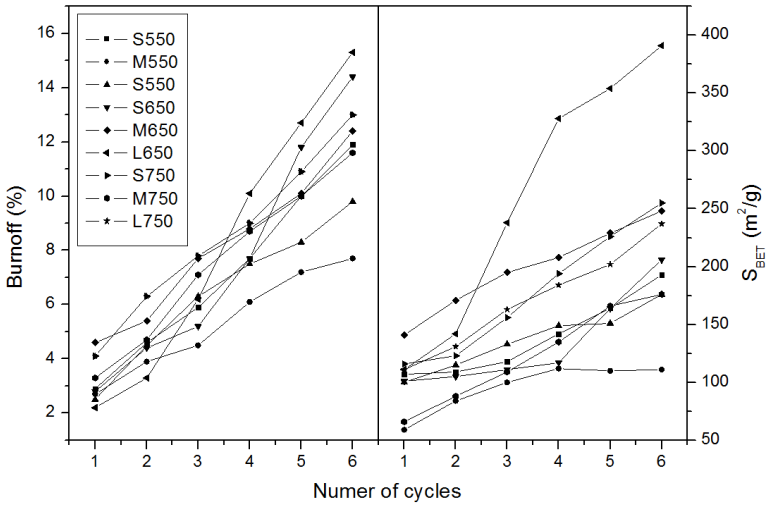



**Figure 1.** Burn-off and $S_{BET}$ vs. number of cycles for 6-cycle tests.

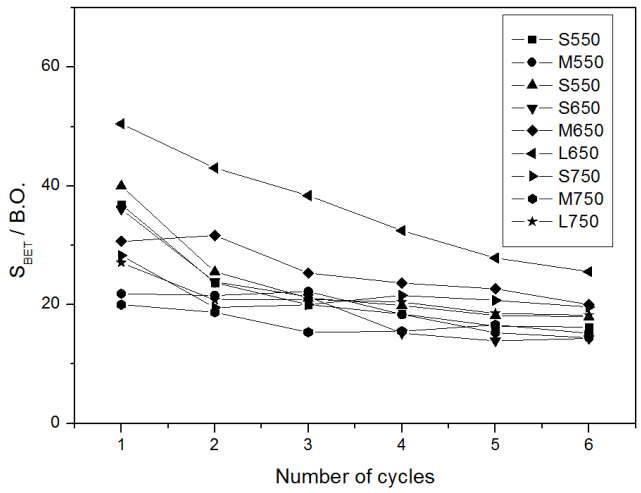



**Figure 2.** Average pore size vs. number of cycles for 6-cycle series.

To analyze more in depth the influence of the particle size and desorption temperature, analysis of variance (ANOVA) was applied to the data of Table 1. The results are shown in Tables 2 and 3.

That the mean effect of desorption temperature on burn-off, i.e., the average effect of increasing the desorption temperature from 550 to 750ºC, is an increase of 3.4 percent units of burn-off, being the statistical significance higher than 95%. The high significance of the quadratic effect for desorption temperature and its sign indicates a higher burn-off for the runs carried out at an intermediate temperature of 650ºC. This result suggest that the desorption of chemisorbed oxygen at 650ºC provides a better regeneration of the active sites for the subsequent oxygen chemisorption step, leading to a higher accumulated burn-off after 6 cycles. The main effect of particle size shows a slight reduction of burn-off when increasing the particle diameter, although the significance for this effect is only 87%.

**Table** 2. Effects of the activation variables on burn-off and porosity development upon the range tested.

| | Burn-off (%) | $S_{BET}$ ($m^2/g$) | Mean Pore Size (nm) |
|---|---|---|---|
| **Average** | 12.2 ± 0.2 | 239 ± 3 | 20.9 ± 0.1 |
| **Effect of the particle diameter (A)** | -1.1 ± 0.2 | 50 ± 5 | -1.2 ± 0.2 |
| **Effect of the desorption T (B)** | 3.4 ± 0.2 | 63 ± 5 | -2.6 ± 0.2 |
| **2nd order effect A·B** | 0 ± 0.3 | -1 ± 6 | -0.4 ± 0.3 |
| **2nd order effect A·A** | 5.5 ± 0.4 | 129 ± 7 | -19.9 ± 0.4 |
| **2nd order effect B·B** | -4.9 ± 0.4 | -181 ± 7 | 17.6 ± 0.4 |

**Table 3.** Statistical parameters associated to the effects of the activation variables on burn-off and porosity development upon the range tested.

| | Burn-off | | $S_{BET}$ | | Mean Pore Size | |
|---|---|---|---|---|---|---|
| | F-ratio | P-value | F-ratio | P-value | F-ratio | P-value |
| **Particle diameter (A)** | 22.69 | 0.13 | 117.19 | 0.06 | 28.52 | 0.12 |
| **Desorption T (B)** | 221.02 | 0.04 | 184.08 | 0.05 | 126.75 | 0.06 |
| **AB** | 0.00 | 1.00 | 0.01 | 0.95 | 2.00 | 0.39 |
| **AA** | 218.29 | 0.04 | 302.01 | 0.04 | 2859.87 | 0.01 |
| **BB** | 177.12 | 0.05 | 599.09 | 0.03 | 2251.34 | 0.01 |
| **Lack-of-fit** | 13.23 | 0.20 | 144.20 | 0.06 | 548.57 | 0.03 |

**Note:** degrees of freedom for effects and lack-of-fit are 1 and 3 respectively.

The effect of desorption temperature on $S_{BET}$ shows trends in accordance with the results for burn-off. Thus, the mean effect of desorption temperature is an increase of the $S_{BET}$ with increasing temperature (significance 95%) up to an intermediate temperature of 650ºC when a maximum occurs. However, the curvature for $S_{BET}$ is more marked than for burn-off. This result indicates that a desorption temperature of 650ºC not only provides a better regeneration of active sites, but also a progressive generation of active sites at inner locations within the char structure. Therefore, at 650ºC burn-off takes place with higher selectivity towards pore generation. In the case of $S_{BET}$, the main effect of particle diameter is significant (94%) and its magnitude is equivalent to that of the desorption temperature. It can be observed that $S_{BET}$ is generated more easily for the largest particles whereas minimum values are obtained for intermediate particle size.

The mean pore diameter after the 6-cycle tests is strongly influenced by the desorption temperature, the main effect of this variable being a reduction of the mean pore size with increasing desorption temperature up to 650ºC where a minimum occurs. This result is in accordance with the enhanced generation of $S_{BET}$ at this temperature. The ANOVA shows a decrease in mean pore size for higher diameters, however, the significance is low (88%).

The discussion above indicates that the best results in terms of burn-off per cycle and development of $S_{BET}$ can be obtained operating within the high range of desorption temperature (650-750ºC) and for extreme particle size (S - L). It must also be pointed out that no interaction or synergy between desorption temperature and particle size was observed. Therefore, for the following series of long duration experiments three combinations of the operating variables were selected: L650, S750 and L750.

Figure 3 shows the results of burn-off and $S_{BET}$ surface area for the series of experiments of 20-cycle duration. The burn-off values were comprised in the range between 32 and 46%, showing a nearly linear dependence on the number of cycles applied for samples S750 and L750, whereas for sample L650 a decrease of the slope is observed beyond burn-off values around 35%. Likewise, the increase of burn-off in each cycle is significantly higher at 650ºC. When different particle sizes are compared at the same desorption temperature (750ºC) the burn-off observed is higher for the smaller particles. The differences in burn-off were relatively small in the first 4-6 cycles and from then became more important.

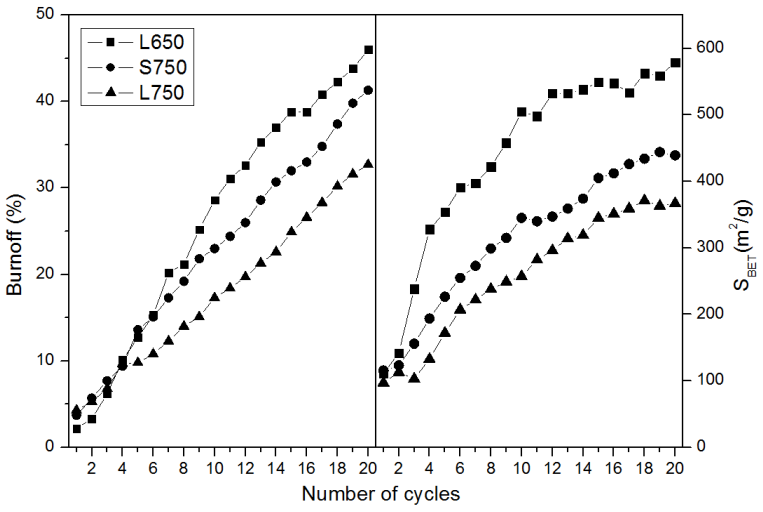



**Figure 3.** Burn-off and $S_{BET}$ vs. number of cycles for 20-cycle tests.

As in the case of burn-off, the $S_{BET}$ values increased with the number of cycles although a progressive saturation effect can be observed as commonly occurs in activation processes. The best results in terms of surface area development were obtained with the largest particles (3 mm) at 650ºC desorption temperature (L650). It is noticeable the substantially higher development of $S_{BET}$ within the third to sixth cycle of that series as compared with the two other in spite of the fact that equivalent burn-off values are obtained up to that point specially with respect to the S750 series.

The important differences on the relative development of surface area of the L650 series in comparison with the two other can be better seen in Figure 4, where the $S_{BET}$/burn-off ratio versus number of cycles is depicted. After 7 – 8 cycles that ratio becomes fairly close for the two series

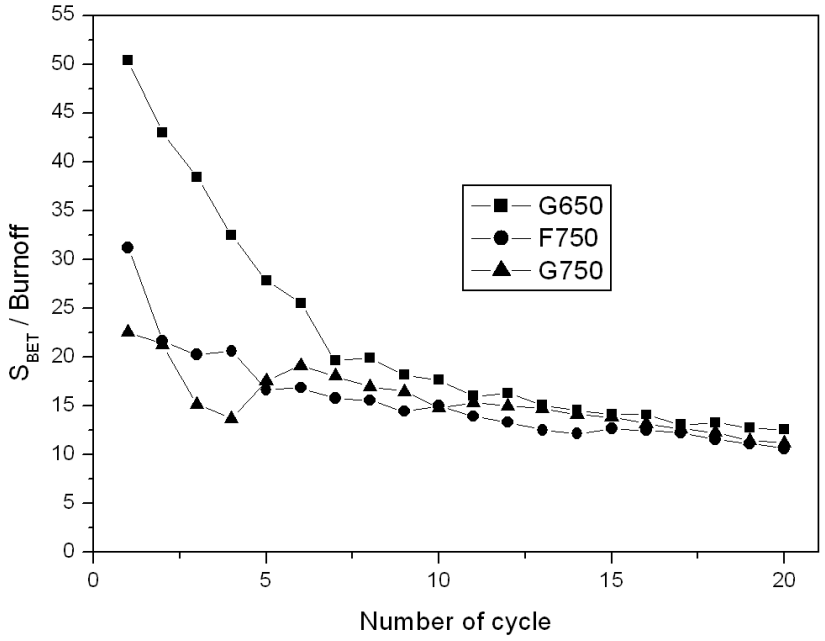



**Figure 4.** Variation of $S_{BET}$/burn-off versus number of cycles.

The mean pore size after 20 activation cycles was very similar for the three series (see Figure 5). During the first 4-6 cycles an important decrease of the mean pore size took place, which was faster for the L650 series, in accordance with the development of surface area. After few activation cycles (4 – 6) the mean pore size decreased slowly up to around 10 nm after completion of the 25-cycles activation.

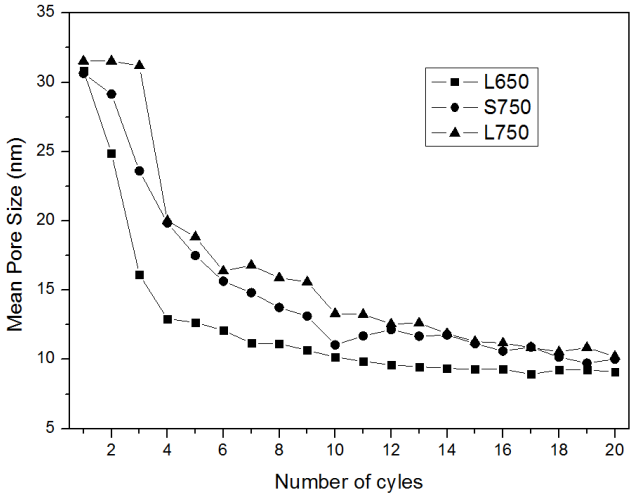



**Figure 5.** Average pore size vs. number of cycles for 20-cycle series.

As can be observed in Figure 6, the beginning of microporosity development depends on the operating conditions. For the largest particle size and 650ºC desorption temperature the microporosity became measurable after the third activation cycle and increased steadily up to cycle 17. On the contrary, at least 6 and 10 activation cycles were needed for some microporosity development in S750 and L750 series, respectively. In all the cases a fairly low micropore volume was obtained On the opposite the development of mesoporosity occurred since the first activation cycle and significant mesopore volume values were achieved thus explaining the early development of surface area. The mesoporosity falls mostly within contribution of narrow mesoporosity (2 – 8 nm). Beyond the 6 – 10 cycle the incremental development of mesoporosity was very low and increase of $S_{BET}$ is essentially associated to microporosity development

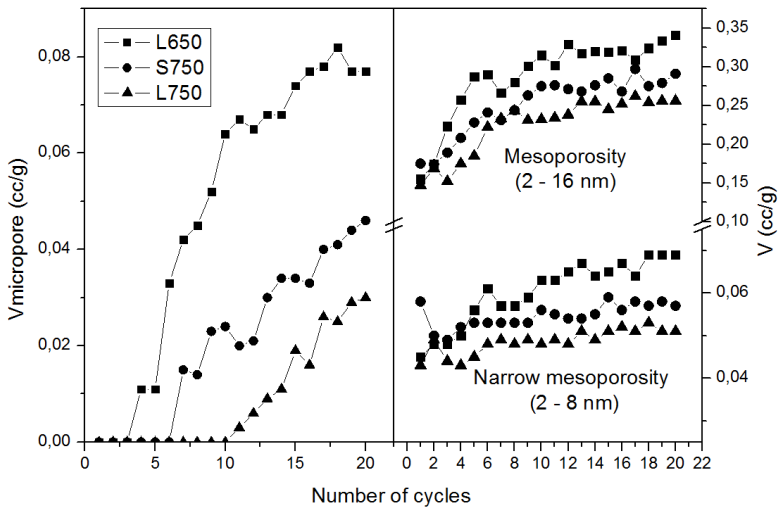



**Figure 6.** Micro, meso and narrow-meso porosity porosity development vs. number of cycles.

According to the results obtained in the first cycles (third to tenth, depending on the operating conditions), mesoporosity is first developed and then micropores are created. This development pattern can be related to the presence of different types of carbon in the initial char, i.e, the different carbon domains of the original carbon black in the waste rubber and those from the carbonaceous material formed during the thermal decomposition of the rubber. In general carbon blacks are less reactive and are mainly embedded in the carbonaceous material obtained from tyres [6] (Donnet, 1982). Therefore, the carbonaceous material from rubber can be expected to react more easily with oxygen and in earlier cycles than carbon black, being responsible for the formation of wider pores.

To learn on the presence of carbon domains of different reactivity TPO analysis of waste tyres char and 20-cycles activated samples was carried out. Figure 7 shows that the TPO profiles are characterized by a rather narrow range of oxidation temperatures, which can be

interpreted as a catalytic effect of the ash components of the samples (Zn, Ca, etc). However, significant differences can be observed among the samples studied. The initial char shows well defined peaks that account for most of the carbon dioxide evolved during TPO analysis: two peaks between 520-525 ºC and a more important peak with a shoulder around 540 ºC. Smaller peaks in the initial char between 550-570 ºC disappeared and displaced to higher temperatures after activation. The application of 20 activation cycles led to the complete removal the most reactive carbon of the initial char, i.e. that evolving as $CO_2$ at 520 and 525ºC. This observation can be associated to the common activation pattern during the 4 to 6 first cycles and might be related to the initial development of mesoporosity. After 20 cycles the TPO of the samples showed a higher relative weight of somewhat less reactive carbon as burn-off increase. Then, the carbon domains in the initial char evolving before 540ºC in the TPO analysis and that are missing in the activated samples could be responsible for the development of microporosity.

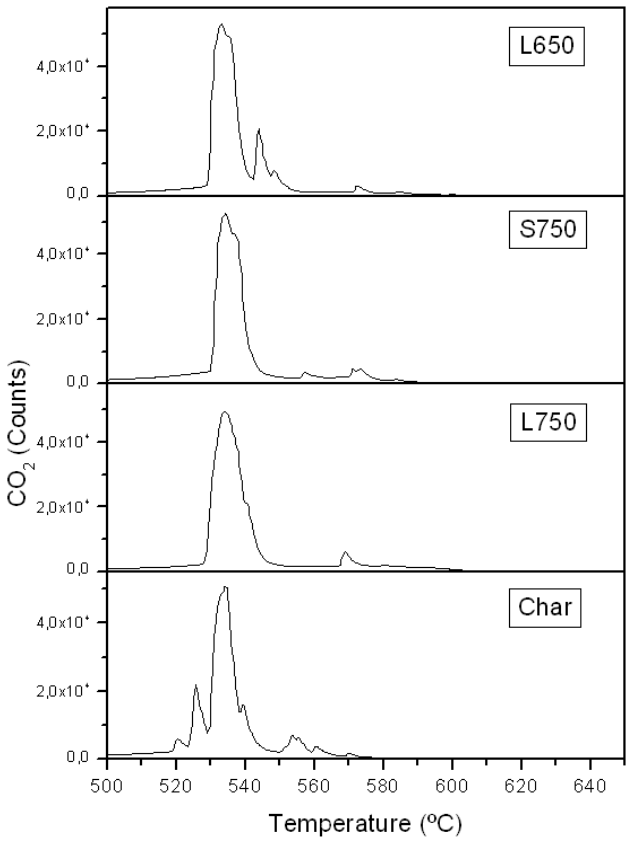



Figure 7. TPO profiles of the initial char and the 20-cycles activated samples.

If the results of $S_{BET}$ vs. burn-off are compared with those obtained by other authors from physical activation of waste tyre chars with steam [1, 7-16], $CO_2$ [1,2,7,8,15-19]or steam-$CO_2$ mixtures [20] and from physico-chemical activation with steam and HCl [11,21] it can be concluded that the surface area values obtained by oxygen chemisorption-desorption are moderate but they are achieved at low burn-off values and a high $S_{BET}$/burn-off ratio (Figure 8). This is a very interesting aspect because low burn-off values implies low destruction of the initial char particle so the method permits the preparation of granular activated carbons.

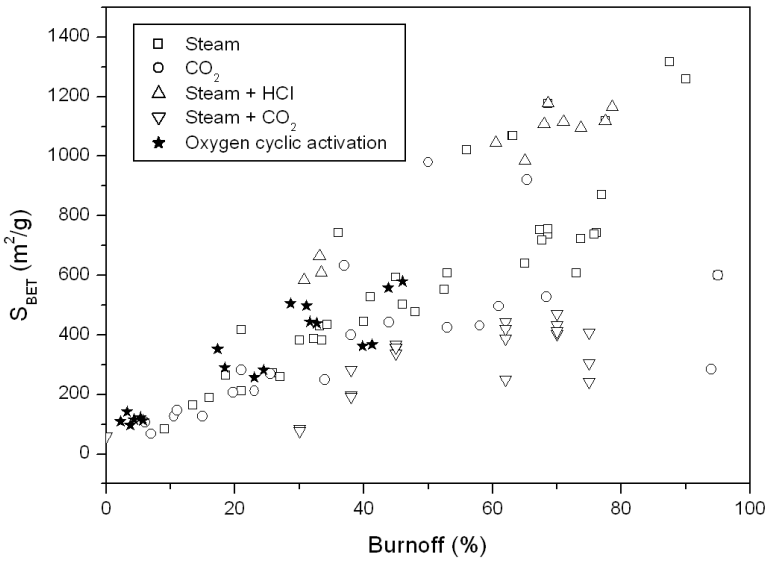
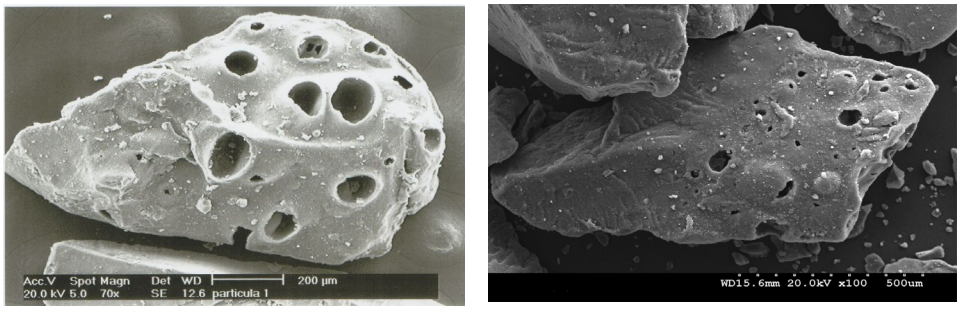



**Figure 8.** Comparison of $S_{BET}$ vs. burn-off for oxygen cyclic activation (current work) and literature data

Figure 9 shows that the morphology of initial char particle is not significantly altered by the treatment even after 20 activation cycles due to the relatively low burn-off value achieved, which makes possible to obtain granular carbons. The activation by cyclic oxygen chemisorption-desorption can overcome the problems related to the high reactivity of waste tyres char with oxygen providing porosity development and porous structure tailoring. Homogenous development of porosity is expected since the chemisorption step avoids activation under oxygen-diffusion limitations.




Initial char particle G650, 20 cycles, B.O.=46%,

**Figure 9.** SEM images of the initial and activated char particle.

## 4. Conclusions

The activation procedure proposed based on cyclic oxygen chemisorption-desorption improves substantially the expectations to prepare activated carbons using air as activating agent avoiding high burn-off. The $S_{BET}$ / burn-off ratios obtained are higher than most of results reported in literature for physical activation. $S_{BET}$ values around 500 $m^2/g$ can be achieved at burn-offs of about 30%, and close to to 600 $m^2/g$ at around 45% burn-off. The surface area values can be considered relatively high bearing in mind that are mainly mesoporous carbons, with a mean pore size around 10 nm. The low burn-off values obtained make possible to prepare granular activated carbons because of the low destruction of the initial particle. This material could have a potential interest as a good catalyst support and/or adsorbent for liquid phase applications. The presence of some metallic species (mainly ZnO) in the ash matter and their efficient removal depending on eventual applications of the resulting activated carbons needs further research.

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